

Fat-Based Surface-Active Agents

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SURFACE-ACTIVE agents, or "surfactants," is a general term applied to organic compounds which, in dilute aqueous solution, considerably lower the surface tension of water, and the interfacial tension of the aqueous solution against a refined mineral oil. The magnitude of this lowering is shown in Figure 1 (11). Most surfactants at 0.1% concentration at 25° lower the surface tension of water from 72 to about 28 to 40 dynes per cm. Surface and interfacial tension values for the majority of surfactants fall within the respective shaded areas of Figure 1.



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Surface-active agents may have emulsification, wetting, spreading, foaming, and detergent properties which make them useful; they may show other useful properties related to surface energy; or, as in the case of the cationic bactericidal agents, their use may appear to be only incidentally related to surface-active properties.

¹A laboratory of the Eastern Utilization Research Branch, Agricultural Research Service, U. S. Department of Agriculture.

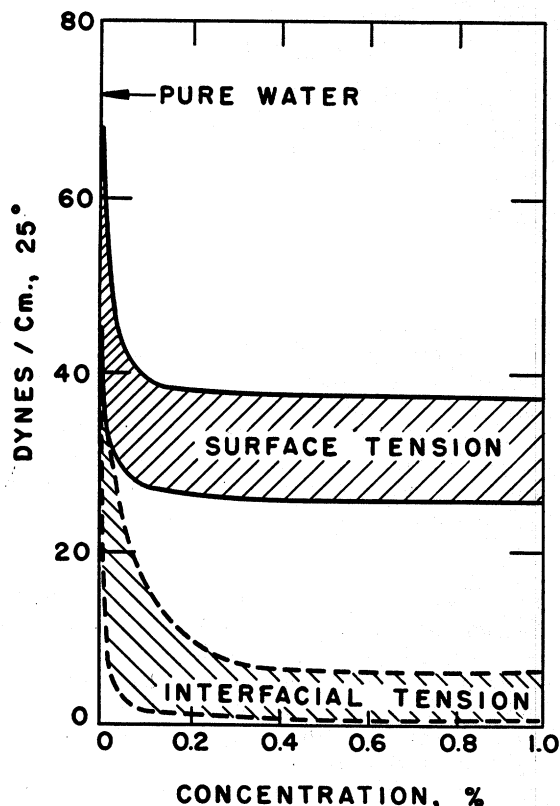


Fig. 1. Surface and interfacial tension values for the majority of surface-active agents (11).

Surface-active agents generally have molecular weights in the range of about 280 to 450. Particularly in the case of fat-based surfactants, the molecule is considerably longer than it is wide. A surface-active agent has a structure combining an essentially hydrophobic nature with atoms or groups predominantly hydrophilic. The hydrophobic part is typified by the paraffinic chain of the higher fatty acids. The hydrophilic part may be a carboxylic, sulfuric, or sulfonic acid group in the case of an anionic surfactant; the $-\text{NH}_3^+\text{Cl}^-$ portion of $[\text{RNH}_3]^+\text{Cl}^-$ in the case of a cationic surfactant; or a series of ether oxygen atoms in the case of nonionic surfactants.

Surface-active agents are roughly classified as the wetting-agent type (with a structure such as $\text{RCHOSO}_3\text{NaR}'$, where R and R' are hydrophobic parts); or the detergent type, such as $\text{RCH}_2\text{OSO}_3\text{Na}$, with the hydrophilic part at or near the end of a hydrophobic chain. The term "surface-active agent" is therefore more inclusive than "wetting agent" or "detergent"; it is a generic rather than a specific term.

The U. S. production of surface-active agents in 1952 is shown in Table I (53). Soap is excluded from

TABLE I
U. S. Production of Surface Active Agents (53)^a
Anionic Surfactants

Item	Cyclic	Production pounds
1	Dodecylbenzenesulfonic acid type.....	307,242,000
2	Sulfonated petroleum aromatic cpds.	84,510,000
3	Sulfated and sulfonated phenyl ethers, substituted biphenyls, sulfonated lignin derivatives.....	49,076,000
4	Sulfonated naphthalene derivs.	5,683,000
Acyclic		
5	Sulfated and sulfonated alcohols.....	112,507,000
6	Sulfated and sulfonated oils, fats, and waxes.....	51,640,000
7	Sulfated and sulfonated esters.....	13,174,000
8	Non-sulfonated salts of fatty acids.....	4,746,000
9	Sulfated and sulfonated nitrogen cpds.	4,181,000
10	Sulfated and sulfonated acids.....	3,285,000
11	Phosphorus cpds.	602,000
	Total anionic surfactants.....	636,646,000
Cationic Surfactants		
12	Cyclic, non-sulfonated, nitrogen cpds.	4,238,000
13	Acyclic, non-sulfonated, nitrogen cpds.	37,027,000
	Total cationic surfactants.....	41,265,000
Nonionic Surfactants		
14	Cyclic, non-sulfonated, ethers and esters.....	26,894,000
15	Acyclic, non-sulfonated, ethers and esters.....	36,342,000
	Total nonionic surfactants.....	63,236,000

^a Soap is excluded in the tabulation. The figures are for 100% active ingredients, not including water, builders, or other additives.

this tabulation, and the figures are for the 100% active ingredient. Most commercial surfactants are however marketed as liquids, powders, pastes, flakes, or spray-dried pellets in which the surface-active agent may be present to the extent of about 25% by weight.

The total production of surface-active agents was 741,147,000 lbs. on a 100% active basis. In a simplified proportion the production of anionic (636,646,000), cationic (41,265,000), and nonionic (63,236,000) surface-active agents was in the relation of 31:2:3, respectively. Anionic surfactants, particularly the dodecylbenzenesulfonic acid type, are the most important in volume of production. The cyclic compounds are, in general, of petroleum or coal tar

origin; the acyclic compounds, in general, are fat-based. The cyclic cationic surfactants may include compounds based on fatty acids. From Table I the total surfactant production of all that might be assumed to be based on fats or fatty acids was about 80% of the figure for the dodecylbenzenesulfonic acid type.

The naturally occurring fats, and more specifically the fatty acids such as lauric, myristic, palmitic, stearic, oleic, and ricinoleic acids, are particularly suitable as a raw material for preparing surface-active agents. The long straight chain $\text{CH}_3(\text{CH}_2)_{10-18}$ and the chains $\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7$ and



are natural sources for the hydrophobic part. The carboxyl group lends itself readily to reactions for the introduction of the necessary hydrophilic part. Hydrophilic groups can also be introduced at the double bond of oleic acid or at the hydroxyl group of ricinoleic acid. A greater variety of surface-active agents has been derived from the fatty acids than from any other single source.

Soap is the oldest known and the simplest surface-active derivative of the fatty acids. Soap has a long history of acceptability and is especially suited for toilet use and for detergency in soft water. Soap has however two major serious defects. It cannot function in acidulated water because it is converted to the almost insoluble fatty acid. It cannot perform well in very hard water because of the precipitation of calcium and magnesium soaps. These defects have led to the development of synthetic detergents. Sales of built synthetic detergents surpassed soap for the first time in 1953; 53% of the total (as marketed) against 47%, respectively (49).

Surface-active agents which do not have the important defects of soap can be made from the same source material as soap, the naturally occurring fats and oils and the derived fatty acids. The most popular fatty acids, in general, have been the coconut oil fatty acids (principally lauric and myristic acids), and oleic acid, which produce more readily soluble surface-active agents than do palmitic and stearic acids. Palmitic and stearic acid derivatives may however have other advantages, such as contributing to better detergency. A difference in solubility may not be an important factor, and economic considerations may be most important. Differences in the solubility of surface-active derivatives of individual fatty acids may not be important when commercial surfactants are made from a mixture of fatty acids. Mutual solubilization may occur to some extent, as it does in soaps.

Examples of fat-based surface-active agents are the following: sulfated and sulfonated oils, fatty acids, esters, and amides; sulfated coconut oil alcohols and sulfated tallow alcohols; sulfated monoglycerides, tallow-based N-methyl taurates and related compounds; fatty acid esters of condensation products of anhydrosorbitols and ethylene oxide; fatty acid alkanolamides; and the quaternized and nonionic derivatives of long chain fatty amines and fatty acid amides.

Fat-based surfactants will be discussed under the usual categories: anionic, cationic, and nonionic, represented by formulas such as $\text{RCH}_2\text{OSO}_3\text{Na}$,

$[\text{RN}(\text{CH}_3)_3]^+\text{Cl}^-$, and $\text{RCH}_2\text{O}(\text{C}_2\text{H}_4\text{O})_x\text{C}_2\text{H}_4\text{OH}$, respectively.

Fat-Based Anionic Surfactants

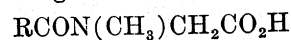
The fat-based anionic surfactants are primarily either sulfates or sulfonates, although carboxylates, sulfites, thiosulfates, persulfates, and phosphates can also be made.

Carboxylic Anionic Surfactants

The simplest carboxylic fat-based surfactant is, of course, soap. Lithium, ammonium, substituted ammonium, alkaline earth, and heavy metal soaps can be made as well as the more common sodium and potassium soaps. The reader is referred to the proceedings of the July 1952 short course on soaps and synthetic detergents (1) and to the paper on metallic soaps of the present series.

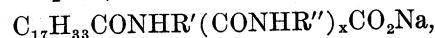
Intermediate amide linkages between the paraffinic chain and the carboxyl group increase the solubility and lime resistance of carboxylic surfactants. Because of their close relation to soap, desirable properties, such as good detergency for cotton, mildness on the human skin, and favorable emulsification characteristics, may be expected.

Products of the general formula



from the condensation of sarcosine, $\text{CH}_3\text{NHCH}_2\text{CO}_2\text{H}$, with a fatty acid chloride have been marketed as the Medialans² (4, 7, 16). Sarcosine can be made from CH_3NH_2 , CH_2O , and HCN . The fatty acyl sarcosinates are soluble detergents, useful except in the very hardest waters, favored for personal use because of their mild feel and good foaming properties. Sodium N-lauryl sarcosinate is an ingredient in a toothpaste composition.

The Lamepons, such as



are made by the reaction of fatty acid chlorides with amino acids from protein hydrolysates (31). They are emulsifiers, softening agents, lime soap dispersing agents, and useful in shampoos and cosmetics. The Maypons are similar products.

Fat-Based Sulfates and Sulfonates

Sulfated and sulfonated fat-based anionic surfactants include the following: "sulfonated" oils, fatty acids, esters, and amides; sulfated alcohols; sulfated monoglycerides; sulfated alkanolamides; sulfated nonionics; α -sulfonated acids; sulfoethyl esters (Igepon A); sulfoethyl amides (Igepon T); sulfoacetates; and ring sulfonated long chain aromatic compounds. From Table I it is apparent the two most important types are the sulfated alcohols and the sulfonated oils.

Sulfonated Oils

The so-called sulfonated oils were the earliest modification on soap. The reaction, under the usual sulfation conditions with sulfuric acid, is predominantly sulfation at the carbon to carbon double bond. The double bond can migrate under the sulfation conditions, to increase the complexity of the reaction (39, 41). Sulfation is mainly at the hydroxyl group in the case of castor oil and the ricinoleates. Other reactions taking place in the sulfation of oils are the partial hydrolysis of the glyceride; partial hydrolysis

²Mention of any product by commercial name does not imply endorsement by the U. S. Department of Agriculture over those of a similar nature not mentioned.

of the sulfated oil to hydroxy acids; lactone, lactide, and estolide formation; and the formation of highly oxidized or polymerized products of unknown constitution (5). Sulfonation rather than sulfation may predominate under anhydrous conditions at somewhat higher temperatures, with chlorosulfonic acid or oleum, or by the use of sulfur trioxide at lower temperatures.

Completely saturated fats or fatty acids cannot be sulfated with sulfuric acid. Oils with a high content of dioenoic or polyenoic acids are likely to polymerize or oxidize under sulfation conditions to give dark, gummy products. The desired oils for sulfation are those containing a sufficient content of oleic or ricinoleic acid, lesser amounts of fully saturated glycerides, and minor amounts of polyunsaturated constituents. A large number of natural fats and oils can be sulfated to give technically useful products. Tallow, castor oil, olive oil, and teaseed oil have been widely used, and a number of other oils can be sulfated.

The oil or fat is usually sulfated with concentrated sulfuric acid at about room temperature, allowed to stand, and washed with aqueous sodium chloride or sodium sulfate to remove the spent acid, leaving the oil as an upper layer. After neutralization the sulfated oil is a yellow to dark brown viscous liquid. Depending on the type of oil and degree of sulfation, it may give a clear foaming solution in water or it may form a cloudy oily dispersion. Sulfation is incomplete, and the product contains unsulfated glyceride and fatty acid, water, and salt, as well as by-products already discussed.

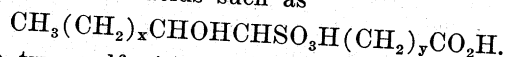
Higher degrees of sulfation to increase solubility and general surface activity can be obtained by extraction and removal of unsulfated material, or by sulfation at about 0° with excess sulfuric acid, oleum, or chlorosulfonic acid. A high degree of sulfation is not required or even desirable when the product is a textile lubricant. High degrees of sulfation are not possible when the oil or fat (tallow, for example) contains a relatively high percentage of unsulfatable saturated fatty acids.

The principal uses for the sulfated oils are in the leather and textile industry. Sulfated cod liver oil, neat's foot oil, and tallow are used in the fat-liquoring of leather. Sulfated tallow is a non-substantive softening agent for cotton and rayon. Sulfated oils have a number of miscellaneous uses as wetting, dispersing, and emulsifying agents. They are not ordinarily classed as detergents. Their structure, $\text{CH}_3(\text{CH}_2)_x\text{CHOHCHSO}_3\text{Na}$, is that of a wetting agent rather than a detergent.

The fatty acids, esters, and amides can be sulfated instead of the glycerides. Sulfated oleic and ricinoleic acids have much greater wetting and foaming power than the sulfated glycerides. Sulfated lower alkyl oleates and ricinoleates are rewetting and soft-

tening agents (27). Sulfated amides are stable to use at high temperatures, in the presence of acid or alkali, and resistant to hard water. Humectol CX (or Dismulgan V), the sulfated diisobutyl amide of oleic acid, $\text{CH}_3(\text{CH}_2)_x\text{CHOSO}_3\text{Na}(\text{CH}_2)_y\text{CON}(\text{C}_4\text{H}_9)_2$ (16, 37) is a wetting and leveling agent, also a versatile textile assistant.

The reaction of oleic acid with oleum or chlorosulfonic acid, in the presence of a solvent, produces hydroxysulfonic acids such as



These true sulfonic acids are stable in hot mineral acid solutions.

Sulfated Fatty Alcohols

The sulfates of the long chain primary alcohols, $\text{RCH}_2\text{OSO}_3\text{Na}$, first introduced about 1930, are the most important fat-based, surface-active agent, as is evident from Table I. The fatty alcohols can be obtained from the saponification of natural waxes, such as those of sperm oil; by the sodium reduction of glycerides or esters (14, 19); and by hydrogenolysis of glycerides, esters, or fatty acids.

The sodium reduction process does not affect unsaturation present in the original glyceride or ester. Except under certain conditions (36, 38) catalytic hydrogenolysis may saturate double bonds.

Sodium reduction of fats gives a sodium hydroxide-glycerol solution which does not permit glycerol recovery. Transesterification of the fat with the reducing alcohol, $\text{CH}_3\text{CHOHCH}_2\text{CH}(\text{CH}_3)_2$, prior to reduction, permits glycerol recovery. Another method is the reaction of the sodium alcoholates with urea, instead of water, to give sodium cyanate as a by-product. Glycerol can then be recovered by water-washing (2).

The fatty alcohols to be sulfated may be those from coconut oil, tallow, or sperm oil. Coconut oil on conversion to long chain primary alcohols would give a mixture of about 15% octanol and decanol, 45% dodecanol (or lauryl alcohol), 18% tetradecanol (or myristyl alcohol), and 22% cetyl, stearyl, and oleyl alcohols. Tallow would give a mixture of about 6% myristyl, 25% cetyl, 14% stearyl, 50% oleyl, and 2% linoleyl alcohols. If the double bond becomes saturated during hydrogenolysis or if the starting material is the completely hydrogenated fat, there will be a corresponding increase in the stearyl alcohol content and a disappearance of oleyl alcohol and other unsaturated alcohols.

The saturated alcohols can be sulfated with an excess of concentrated sulfuric acid, with chlorosulfonic acid, or with sulfur trioxide. Sulfation with sulfuric acid is usually incomplete and is accompanied by a certain amount of dehydration and olefin formation. Small amounts, about 5%, of unsulfated matter and

TABLE II
Surface Active Properties of Sodium Salts of Sulfated Alcohols (56)

	Surface tension, 0.1%, 25°, dynes/cm.	Interfacial tension, 0.1%, 25°, dynes/cm.	Foam height, 0.1% solns., 100 p.p.m., 60° mm.	Sinking time, 0.1% solns., 25°, seconds	Detergency, 0.1% solns., 100 p.p.m., 60° ΔR	Solubility %, 25°
dodecyl sulfate.....	49.0	20.3	240	13	28.6	28.8 (56)
tetradecyl sulfate.....	25.3	9.1	246	12	34.2	0.237 (56)
hexadecyl sulfate.....	35.0	7.5	178	59	35.9	0.05 (9)
octadecyl sulfate.....	40.6	14.2	151	280	38.6	0.02 (17)
oleyl sulfate.....	35.0	7.4	226	19	37.1	easily soluble
lauryl-sulfate.....	36.1	6.3	202	20	37.6	easily soluble

impurities generally have no detrimental effect. Extraction of impurities by carbon tetrachloride or gasoline may be necessary.

When a product substantially free of inorganic salts is desired, the reaction mixture prior to neutralization may be separated into two layers by adding butanol or carbon tetrachloride. The lower layer of spent sulfuric acid is withdrawn. After neutralization and solvent removal the product contains only minor amounts of inorganic salt.

Sulfated primary fatty alcohols may be marketed as the sodium salt in dry form or as an aqueous paste, associated with trade names such as Avitex, Duponol, Gardinol, Lissapol, Maprofix, Modinal, Orvus, and Stepanol. Large amounts of the triethanolammonium salt are made for use in shampoos and liquid detergents. Sulfated alcohols are stable to alkaline hydrolysis but can be hydrolyzed to the long chain alcohol in hot acid solutions.

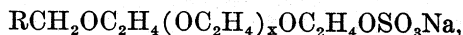
The individual sodium alkyl and alkenyl sulfates compare as shown in Table II (56). The surface tension value for sodium dodecyl sulfate at concentrations near the critical micelle concentration (about 0.25%) is 37.4. The high surface and interfacial tension values for sodium octadecyl sulfate are probably due to incomplete solution. Sodium dodecyl sulfate is not as good a detergent at 60°. Sodium oleyl sulfate and sodium elaidyl sulfate are good detergents readily soluble at room temperature.

The sulfation of oleyl alcohol is complicated by the ease with which the usual sulfating agents cause reactions to take place at the double bond as well as at the hydroxyl group. The purity of sodium oleyl sulfate and sodium elaidyl sulfate, estimated by the iodine number, is generally related to better values in the measurement of foaming, wetting, and detergent properties (56). Moderate sulfating agents, such as the following, are at least partially successful in minimizing reactions involving the double bond: pyridine-sulfur trioxide; sulfamic acid; dioxane-sulfur trioxide; complexes of sulfur trioxide or chlorosulfonic acid with inorganic salts; and complexes of urea with chlorosulfonic acid or sulfuric acid.

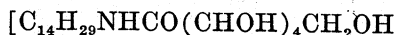
The sulfated fatty alcohols are detergents, foaming, wetting, dispersing, and emulsifying agents. They can be used in light and heavy duty laundering, dishwashing, shampoos, brushless shaving creams, toothpastes, and metal cleaning and are assistants in the textile and leather industries. Other uses are in the preparation of cosmetic creams, in emulsion polymerization, in disinfectants, fungicides, germicides, herbicides, and insecticides, in flotation compositions, and in the treatment of gastric and duodenal ulcers.

Fat-Based Sulfates with Intermediate Linkages

Fat-based sulfates with an intermediate linkage can be formed from fatty acids, alcohols, and amines. Products from fatty acids are the sulfated monoglycerides, $\text{RCO}_2\text{CH}_2\text{CHOHCH}_2\text{OSO}_3\text{Na}$, and sulfated ethanolamides, $\text{RCONHC}_2\text{H}_4\text{OSO}_3\text{Na}$, from the reaction of a fatty acid with ethanolamine and subsequent sulfation. Sulfated nonionics,



are made from the fatty alcohols. An example of a product from a fatty amine is the sesquisulfate of N-tetradecyl-D-gluconamide



sulfated to an average of 1.5 sulfate groups in the molecule (24)].

The sulfated monoglycerides of coconut oil can be made by sulfation of the crude monoglyceride or by simultaneous esterification of glycerol with fatty acid and sulfuric acid in a continuous process (29). Sulfated monoglycerides are sufficiently stable to hydrolysis to be used in household cleaning and washing and in most commercial processes involving surfactants, but are hydrolyzed at the carboxylate linkage in hot alkaline solutions and at the sulfate linkage in hot acid solutions. They have been marketed as a light duty household detergent, a synthetic detergent bar (Vel Beauty Bar), and as a textile assistant (Arctic Syntex M).

The sulfated ethanolamide of coconut oil is made by heating equimolar quantities of the fatty acid and ethanolamine at about 170-180° with the removal of water, and then sulfating with sulfuric acid at 30° (30). Oleic, palmitic, and stearic acids are used as well as the coconut oil fatty acids.

Nonionic compounds from the condensation of a long chain fatty alcohol with less than the number of ethylene oxide molecules required for solubility in water can be converted to water-soluble surfactants by sulfation of the terminal hydroxyl group.

Fat-Based Sulfonates

Surface-active agents containing a sulfonate group, $-\text{SO}_3\text{Na}$, have the advantage over those containing a sulfate group, $-\text{OSO}_3\text{Na}$, in greater stability to hydrolysis, particularly in acid solutions. This is not always an important advantage. Other considerations such as inexpensive methods of manufacture and more desirable foaming, wetting, emulsifying, and detergent properties may be more important.

Methods for the direct attachment of a sulfonic acid group to a hydrophobic chain include the following: sulfonation at the double bond; α -sulfonation of saturated fatty acids; double decomposition of sulfates or halides with inorganic sulfites; and the oxidation of polysulfides or mercaptans.

The first reaction has been discussed under the subject of the sulfonated oils. Hydroxysulfonic acids are produced by the reaction of oleic acid and its derivatives with energetic sulfonating agents such as chlorosulfonic acid, oleum, or sulfur trioxide.

Saturated fatty acids can be sulfonated exclusively in the α -position by the addition of liquid sulfur trioxide to a dispersion of the fatty acid in carbon tetrachloride or tetrachloroethylene. The α -sulfonated acids can be isolated and converted to salts, or to car-

TABLE III
Surface Active Properties of Salts of α -Sulfonated
Acids and Esters (52)

	Solubility 40° g./100 ml.	Surface tension, 0.1%, 25° dynes/ cm.	Sinking time 0.1%, 30° seconds	Foam height, 0.25%, 60° mm.	Detergency, 0.25%, 60° %D
Na α -sulfolauric acid.....	0.74	32.7	> 1,000	< 10	23.9
Na α -sulfomyristic acid.....	0.17	30.2	98	160	56.6
Na α -sulfopalmitic acid.....	0.096	176	55.6
Na α -sulfostearic acid.....	0.05	46.4
Na ₂ α -sulfolaurate.....	7.4	69.3	> 1,000	< 10	19.2
Na ₂ α -sulfomyristate.....	1.5	62.8	349	< 10	26.1
Na ₂ α -sulfopalmitate.....	0.45	44.3	45	169	49.5
Na ₂ α -sulfostearate.....	0.14	37	57.7
NH ₄ α -sulfopalmitic acid..	0.5	40.4	100	185	56.1
Triethanolammonium α -sulfopalmitic acid.....	130.00	42.4	77	215	55.4
Na Isopropyl α -sulfostearate.....	15.00	37.6	43	160

boxylic esters by heating with an alcohol in the absence of an esterification catalyst. Some properties of α -sulfonated compounds are summarized in Table III (52, 55, 57).

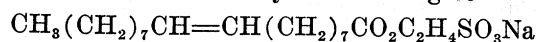
Esters of α -sulfonated acids are readily soluble and unexpectedly resistant to hydrolysis in hot acid solutions. α -Sulfonated esters of secondary alcohols, such as sodium isopropyl α -sulfotesarate, are also stable in hot alkaline solutions. This behavior extends the range of possible application.

The ease with which saturated acids can be mono-sulfonated exclusively in the α -position by an inexpensive process suggests that α -sulfonated acids may be versatile intermediates in the utilization of fats.

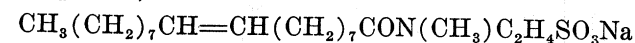
Sodium salts of α -sulfonated fatty acid amides, $RCH(SO_3Na)CONH_2$, $RCH(SO_3Na)CONHCH_3$, and $RCH(SO_3Na)CONHC_6H_5$, have been prepared from the α -bromo compound by reaction with neutral sodium sulfite (26).

Fat-Based Sulfonates with an Intermediate Linkage

Surfactants with an intermediate ester or amide linkage between the hydrophobic chain and the sulfonate group are prepared by the reaction of the acid chloride of oleic acid with sodium isethionate or the sodium salt of N-methyltaurine to give



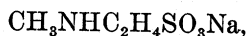
(Igepon A) or



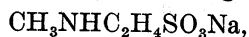
(Igepon T), respectively.

Sodium isethionate, $HOC_2H_4SO_3Na$, is made by the reaction of ethylene oxide with aqueous sodium bisulfite at 70-80° under sufficient pressure to retain the ethylene oxide. The acid chloride is made by means of phosphorus trichloride. A mixture of the acid chloride of oleic acid, dry sodium isethionate, and sodium carbonate is agitated and heated in the molar proportions of 1:1.2:0.1, respectively, to 115°, with the evolution of hydrogen chloride. The reaction mixture is neutralized and ground to a finished product containing 70% active ingredient (4, 16, 37). Similar products can be made from the acid chlorides of palmitic, stearic, and coconut oil fatty acids. The sulfoethyl esters are textile assistants and detergents, sufficiently stable to hydrolysis in neutral, mildly basic, or warm dilute acid solutions but hydrolyzed in hot acid or alkaline solutions.

The sodium salt of N-methyltaurine,



is prepared as an aqueous solution by the reaction of 42% aqueous $HOC_2H_4SO_3Na$ with excess CH_3NH_2 at 280° under a pressure of 200 atmospheres. An aqueous solution, 12,000 lbs., containing 930 lbs. of



is made alkaline with 172 lbs. of 30% NaOH. Technical oleic acid chloride, 2,220 lbs., along with 295 lbs. of 30% NaOH, are added during 4 to 6 hrs. The mixture is heated to 50°, neutralized with HCl, 5,200 lbs. of NaCl are added, and water to bring the total weight to 26,000 lbs. The clear solution is spray-dried to give Igepon T Powder containing about 30% active ingredient (4, 7, 16, 19).

The acyl taurates, first introduced about 1932, are more resistant to hydrolysis than the sulfoethyl esters, particularly in alkaline solutions. They are well es-

tablished surfactants, principally developed as textile assistants, but useful as detergents, lime soap dispersants, in shampoos, the fat-liquoring of leather, metal plating, and in a number of miscellaneous applications. Variations in the acyl and the alkyl group attached to nitrogen are possible as well as variations in the structure $-CH_2CH_2SO_3Na$. An acyl taurate from the acid chlorides of tallow acids is a recent development.

Sulfoacetates of the general formula

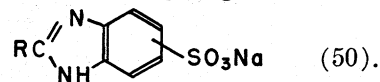


are made by the esterification of oleyl, cetyl, stearyl, or coconut oil alcohols with chloroacetic acid, and replacement of the chlorine atom by reaction with an alkali metal sulfite. Nacconol LAL is the sulfoacetate of coconut oil fatty alcohols. Sulfoacetates are useful in toothpastes, shampoos, and cosmetics.

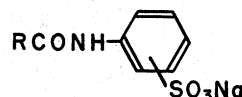
Fat-Based Aromatic Sulfonates

Fat-based surfactants which are both aliphatic and aromatic in nature, and are sulfonated in the benzene ring, can be prepared from fatty acids or fatty acid chlorides. The following are examples: sulfonated benzimidazoles; sulfoarylstearic acids from oleic acid (51); sulfonated alkyl aryl ketones (33); and N-acylaminophenylsulfonic acids.

Sulfonated benzimidazoles used in textile processing are made by condensing o-phenylenediamine with a fatty acid to form a benzimidazole, which is then sulfonated in the benzene ring to give



Compounds of the general formula,



where the benzene ring and the amido nitrogen may be variously substituted, are formally related to Igepon T, with an aromatic ring in place of $-C_2H_4-$. Several such compounds have been prepared and evaluated (47, 54).

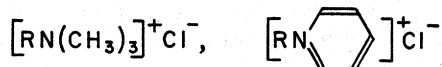
Cationic Fat-Based Surfactants

Cationic surface-active agents have been called "invert soaps." They are just the opposite of ordinary soaps. The hydrophobic part is the cation. Most of the cationic surfactants are fat-based. Fats are a natural and convenient source for the hydrophobic chain. The cationic surfactants are almost exclusively substituted ammonium salts based on amines or amides derived from long chain fatty acids, or on long chain alkyl halides derived from fatty alcohols. The long chain amines, RNH_2 , are almost insoluble in water but soluble in the form of salts or quaternary ammonium compounds. Mixtures of fat-based anionic and cationic surfactants form a neutral insoluble compound and so are incompatible.

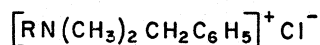
The development of the cationic surfactants has been conditioned by the discovery of uses which are not directly related to surface-active properties such as wetting, foaming, or detergent properties; or the ability to lower surface tension. The important uses are as germicides, fungicides, and disinfectants, water-repellents, softening agents, and the fixation of sul-

fonic acid dyestuffs by union with a long chain cation.

The bactericidal activity of cationic surfactants (8) has been related to their affinity for wool (12) and to the critical micelle concentration of these colloidal electrolytes (6). Fat-based cationic surfactants include structures such as



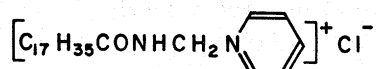
and



Trimethylalkylammonium chlorides and related compounds can be based on tallow acids, converted to nitriles, hydrogenated and methylated (15, 35). Alkylpyridinium halides and related compounds can be based on fatty acids, converted to alcohols, and then to alkyl halides. Maximum bactericidal activity occurs at a long chain alkyl group of 16 carbon atoms (46).

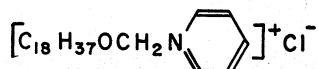
Cationic surfactants are used for many disinfecting purposes: sanitization of fabrics in laundries; sterilization of dishes and glassware in restaurants; and sterilization of instruments and skin in surgery.

Cationic water-repellents are applied to the fabric and caused to decompose with the deposition of a lasting wash-resistant, water-repellent finish. The water-repellent

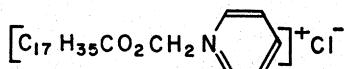


Zelan, from reaction with pyridine, formaldehyde, and HCl (58), represents one of the largest uses for stearic acid amide. It is applied by padding on the fabric, and drying and heating to about 120°, with evolution of pyridine and formation of a thin, firmly adherent coating of $(\text{C}_{17}\text{H}_{35}\text{CONH})_2\text{CH}_2$.

The action of cationic surfactants as water-repellents depends on their instability. An essential structural feature seems to be a methylene group between the quaternary nitrogen atom and an amide, ether, or ester linkage. Two other examples are



(Velan), and



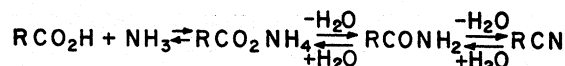
(Norane), made from $\text{C}_{18}\text{H}_{37}\text{OCH}_2\text{Cl}$ and $\text{C}_5\text{H}_5\text{N}$; and from $\text{C}_{17}\text{H}_{35}\text{COCl}$, CH_2O and $\text{C}_5\text{H}_5\text{N}$, respectively.

Cationic softening agents are more effective than anionic softening agents, such as sulfated tallow. They are strongly adsorbed on cotton or rayon at low concentrations and impart a soft, rich hand to the fabric, an effect which resists washing and is semi-permanent. The softening effect is essentially a lubricating action between the individual fibers.

Cationic Surfactants with Nitrogen Joined Directly to the Hydrophobic Chain

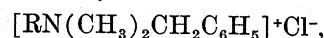
The largest and most important group of cationic surfactants centers on the use of fat-based amines of 8 to 18 carbon atoms.

Fatty acids and ammonia form the ammonium salt and are dehydrated to amides or nitriles depending on the reaction conditions. The equilibria



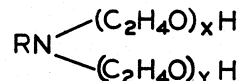
probably do not represent true reaction mechanisms. Nitriles are hydrogenated to amines in the presence of Raney Ni at 150° under 200 lbs. /sq. in. pressure (15, 20, 45). The amines and their salts are widely used for their surface activity, particularly as flotation agents, but principally they are intermediates for the preparation of cationic surfactants. Secondary and tertiary amines such as $\text{C}_{18}\text{H}_{37}\text{NHCH}_3$ and $\text{C}_{18}\text{H}_{37}\text{N}(\text{CH}_3)_2$ are formed by hydrogenation of the nitrile in the presence of CH_3NH_2 ; by the alkylation of $\text{C}_{18}\text{H}_{37}\text{NH}_2$; or the reaction of $\text{C}_{18}\text{H}_{37}\text{Cl}$ with CH_3NH_2 or $(\text{CH}_3)_2\text{NH}$.

Alkyldimethylbenzylammonium chlorides,

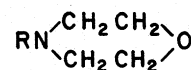


are made by methylation of RNH_2 to $\text{RN}(\text{CH}_3)_2$, which is then quaternized with $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$. The product is associated with trade names such as Roccal and Triton K-60.

More complex groups may be jointed to the nitrogen attached to the hydrophobic chain. The Ethomeens,



from the reaction of ethylene oxide with RNH_2 , are more soluble and less basic the larger the values of x and y. When $x = y = 1$,



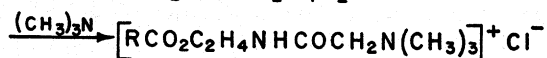
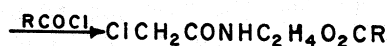
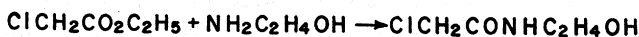
can be formed by dehydration (34). α -Pyridinium derivatives of fatty acid amides, for application in dyeing operations, have been prepared from pyridine and alpha-bromofatty acid amides (25).

Cationic Surfactants with an Intermediate Linkage

Cationic surfactants with intermediate amide, ester, and ether linkages have been prepared.

The Sapamines, useful for color fixation and as softening agents (13), can be prepared from a fatty acid, acid chloride, or ester, and an unsymmetrical dialkyl ethylenediamine. The condensation products, such as $\text{RCONHC}_2\text{H}_4\text{N}(\text{C}_2\text{H}_5)_2$, can be used in the form of a salt, or quaternized with $(\text{CH}_3)_2\text{SO}_4$.

Cationic surfactants with amide and ester intermediate linkages can be made from $\text{ClCH}_2\text{CO}_2\text{C}_2\text{H}_5$, $\text{NH}_2\text{C}_2\text{H}_4\text{OH}$, a fatty acid chloride, and $(\text{CH}_3)_3\text{N}$.



Corresponding pyridinium compounds are bactericides and detergents, but no correlation has been found in the two properties (10).

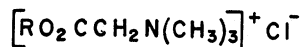
Fatty acids or acid chlorides normally react at the amino acid group of $\text{NH}_2\text{C}_2\text{H}_4\text{OH}$ unless the amino

group is blocked, as it is when $\text{HOC}_2\text{H}_4\text{NH}_2 \cdot \text{HCl}$ is used. Products such as $\text{RCO}_2\text{C}_2\text{H}_4\text{NH}_2 \cdot \text{HCl}$ and



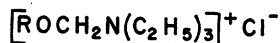
are effective cationic surfactants, hydrolyzed in alkaline solutions, and normally used as the salt in acid solutions.

The simple betaine esters,



are made from a fatty alcohol, $\text{ClCH}_2\text{CO}_2\text{H}$, and $(\text{CH}_3)_3\text{N}$.

Cationic surfactants such as



similar to but more stable than Velan, are made from the chloromethyl ether of a fatty alcohol and $(\text{C}_2\text{H}_5)_3\text{N}$.

Nonionic Fat-Based Surfactants

The most strongly hydrophobic groups are ionogens and most surface-active agents (the anionic and cationic) are ionogens. The nonionic surfactants are not colloidal electrolytes and are incapable of ionizing in aqueous solution.

In general, the raw materials for manufacturing nonionics are ethylene oxide, ethylene oxide derivatives such as polyethylene glycol and diethanolamine, glycerol, and sorbitol, for the hydrophilic part. The principal hydrophobe sources are alkylphenols, tall oil, branched chain alcohols, amines and mercaptans, and the fat-based long chain alcohols, acids, amines, and amides. Nonionics represented about 9% of the total surfactant production in 1952. Nonionics are the newest class and the most versatile in application. It is conceivable that the production of nonionics will continue to grow at a rate greater than all surface-active agents (32).

Nonionic surfactants, with the possible exception of those containing an ester linkage, may be expected to have inherent advantage of stability under almost any condition of use: stability to hydrolysis by acid or alkali; stability to hard or sea water or metal ions; and compatibility with anionic or cationic surfactants. They are also versatile in application through control of the balance between hydrophobic and hydrophilic characteristics. Frequently they can be made and shipped conveniently in anhydrous salt-free form.

Disadvantages of the nonionic surfactants are that most of them are liquids (this may be overcome by formulation with urea, sulfates, phosphates, or borates); they have poor foaming qualities; and they may be more expensive than an equally suitable anionic surfactant.

Fat-based nonionic surface-active agents are detergents, emulsifying agents, foam stabilizers and thickening agents, dispersing agents and solubilizers; and they are useful in dry cleaning.

The reaction of a long chain fatty alcohol with ethylene oxide gives nonionic surfactants of the general formula $\text{R}(\text{OC}_2\text{H}_4)_n\text{OH}$. Starting with oleyl alcohol and adding increasing amounts of ethylene oxide, a useful degree of water solubility is obtained when n is about 6 to 8. These products are suitable for wool processing and for emulsifying neutral oils.

When n is about 10 to 15, the products are good detergents for wool, cotton, and rayon. When n is about 20 to 30, excellent emulsifying agents are obtained.

The manufacture of Leonil OX is described as follows (16): Powdered sodium hydroxide, 80g., is added to 800 kg. of oleyl alcohol in a glass-lined kettle, the mixture is heated to 160-180°, and the kettle is evacuated to 10 mm. pressure. Ethylene oxide from a storage tank holding 2,000 kg. is allowed to flow in under a nitrogen pressure of about 3 atmospheres. The flow is regulated by this pressure. The reaction is highly exothermic and requires about 12 to 14 hrs. for completion. The product, a soft waxy paste, contains about 15 moles of ethylene oxide per mole of oleyl alcohol. It gives a clear solution in cold water which becomes turbid on heating to about 40°, and has been marketed as a 20% or 30% aqueous solution (Peregal O and Leonil O, respectively). A product containing about 25 moles of ethylene oxide (Diazopon A), is not as good a detergent but has been used for a dyeing assistant, particularly effective in minimizing crocking.

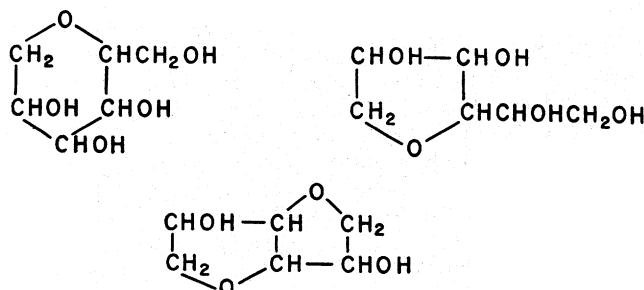
The longer the hydrophobic chain, the more molecules of ethylene oxide are required for adequate solubility. In this respect the alkylphenols from petroleum or coal tar, the coconut oil alcohols, and oleyl alcohol, might be preferred to cetyl or stearyl alcohol. It has been suggested in the case of the saturated alcohols that the number of ethylene oxide molecules required is 3 less than the number of carbon atoms in the fatty alcohol (43). Reaction products with less than the necessary oxyethylene groups can be converted to water-soluble anionic surfactants by sulfation.

The phenomena of inverse solubility (greater solubility in water at lower than at higher temperatures) is characteristic of the nonionics. Decreasing solubility with rise in temperature is due to decreased association of water and solute molecules. The "cloud point," or the temperature at which turbidity first appears, can be correlated with the number of molecules of ethylene oxide, n , condensed with one molecule of the fatty alcohol. The value of n is an average value, and the actual product is never a chemical individual. Some fractionation into species with a limited range in molecular weight may be possible by methods such as vacuum-distillation or differential solubility.

Fatty alcohol-ethylene oxide condensates are effective in washing wool and cotton but are poor foamers in comparison with ionic detergents. They have the advantage of being non-substantive; the aqueous solutions are not depleted or exhausted by adsorption. Sulfation converts them to anionic detergents but preserves their excellent wool washing characteristics, improves cotton detergency and foaming, and economizes on the number of ethylene oxide molecules required. A sulfated product from oleyl alcohol and about 5 moles of ethylene oxide is similar in performance to an unsulfated product from oleyl alcohol and 15 moles of ethylene oxide.

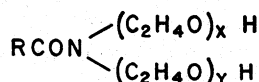
Fatty acid-ethylene oxide condensation products, $\text{RCO}_2(\text{C}_2\text{H}_4\text{O})_x\text{C}_2\text{H}_4\text{OH}$, have the same general characteristics as those from fatty alcohols except that they are hydrolyzed in hot alkaline solutions. The fatty acids may be esterified with polyethylene glycols (3) or condensed with ethylene oxide.

Fatty acids such as lauric, palmitic, stearic, and oleic acid can be esterified with anhydrosorbitols to give emulsifying agents, marketed under the trade name Span. Further reaction of available hydroxyl groups in the esters, with ethylene oxide, increases water solubility and extends the range of application. The polyethenoxylated esters are marketed under the trade name Tween. The anhydrosorbitols have the formulas:



The Tweens are made so that one fatty acid residue is present per mole of anhydrosorbitol.

The Ethomids,



are made by the reaction of a fatty acid amide with ethylene oxide. Control of the nature of R and of the values for x and y gives a range of products versatile in application (27, 42).

An important surface-active agent, generally considered in the nonionic class, is the reaction product from one mole of a fatty acid and two moles of $\text{NH}(\text{C}_2\text{H}_4\text{OH})_2$. From the method of formation the product would be presumed to be $\text{RCON}(\text{C}_2\text{H}_4\text{OH})_2$. The process is extremely simple (21). A mixture of one mole of coconut oil fatty acid and two moles of $\text{NH}(\text{C}_2\text{H}_4\text{OH})_2$ is heated at 150-170° until nearly one mole of water has been recovered and the free fatty acid value has fallen to about 5%. The resulting viscous amber liquid, readily soluble in water with a pH of about 9, has been considered to be a mixed micelle of alkanolamide, amine, and fatty acid (22, 59). The alkanolamides are widely used for their synergism with other surface-active agents. They are foam stabilizers and thickeners for detergents (40), clarifying and emulsifying agents, and they improve the detergency of soap in hard water (59).

Summary

A review of the fat-based anionic, cationic, and nonionic surface-active agents, primarily those useful in aqueous solution, has shown that the natural fats and fatty acids are particularly suitable raw materials. Because of the presence of the hydrophobic chain and of a carboxyl group by means of which hydrophilic character can be imparted, a greater variety of surface active agents have been made from the fatty acids than from any other single source.

The references cited include a text (44) and a symposium (28) on the chemistry and technology of surface-active agents, and indices of trade names with a brief description of the commercial product (23, 48).

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